

## PATENT ABSTRACTS OF JAPAN

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**(54) NONAQUEOUS SECONDARY BATTERY AND ITS MANUFACTURING METHOD**

**(57)Abstract:**

**PROBLEM TO BE SOLVED:** To provide a nonaqueous secondary battery having a high capacity and excellent charge and discharge characteristics, by filling a positive electrode active material at a high filling level.

**SOLUTION:** In the nonaqueous secondary battery having the positive electrode formed by forming a positive electrode mix layer on at least one surface of a positive electrode collector, a negative electrode, and nonaqueous electrolyte, a fluorine nonionic surface active agent is contained in the positive electrode mix. A compound expressed by the following formula (1) ((m) is an integral number of 4-12, (n) is an integral number of 5-30, and R is a low class alkyl group) is preferable for the fluorine nonionic surface agent, and the content of the fluorine nonionic surface active agent in the positive electrode mix is preferably 0.01-1 wt.%.

C<sub>2</sub>-F<sub>10-18</sub>OB<sub>n</sub>N(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>O<sub>m</sub>(CH<sub>2</sub>)<sub>2</sub>OCH<sub>2</sub>CH<sub>2</sub>Cl

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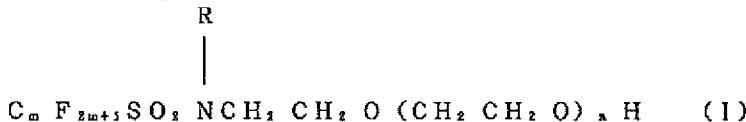
CLAIMS

## [Claim(s)]

[Claim 1]A nonaqueous secondary battery by which a fluorine system Nonion type surface-active agent being included in the above-mentioned positive electrode mixture in a nonaqueous secondary battery which has at least one anode, negative electrode, and nonaqueous electrolyte of a positive pole collector which form a positive electrode mixture layer in a field.

[Claim 2]The nonaqueous secondary battery according to claim 1, wherein a fluorine system Nonion type surface-active agent is a compound expressed with following formula (I).

## [Formula 1]



(As for the integer of 4-12, and n, in m, the integer of 5-30 and R are low-grade alkyl groups)

[Claim 3]The nonaqueous secondary battery according to claim 1, wherein a fluorine system Nonion type surface-active agent contains 0.01 to 1% of the weight in positive electrode mixture.

[Claim 4]The nonaqueous secondary battery according to claim 1 characterized by using polyvinylidene fluoride system resin as a binder of an anode.

[Claim 5]The nonaqueous secondary battery according to claim 1 using at least one sort chosen from a group which consists of a lithium nickel oxide, a lithium cobalt oxide, and a lithium manganic acid ghost as positive active material.

[Claim 6]In manufacturing the nonaqueous secondary battery according to claim 1, at least Positive active material, Add and carry out mixture dispersion of the fluorine system Nonion type surface-active agent to a system containing a binder and an organic solvent, and a positive electrode mixture content paste is prepared, A manufacturing method of a nonaqueous secondary battery producing an anode by applying the positive electrode mixture content paste to at least one field of a positive pole collector, drying and forming a positive electrode mixture layer.

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[Translation done.]

JAPANESE  [JP,2002-075330,A]

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CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION  
TECHNICAL PROBLEM MEANS EXAMPLE

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[Translation done.]

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

#### [0001]

[Field of the Invention] This invention relates to a nonaqueous secondary battery which is high capacity and in which the charge-discharge cycle characteristic was excellent, and a manufacturing method for the same in more detail about a nonaqueous secondary battery.

#### [0002]

[Description of the Prior Art] The demand to the rechargeable battery which has high energy density is increasing increasingly with the miniaturization of electronic equipment, and the spread of cellular phones. Now, as a high capacity rechargeable battery which meets this demand,  $\text{Li}_x\text{CoO}_2$  is used for positive active material and the rechargeable lithium-ion battery using the carbon material as negative electrode active material is commercialized. This rechargeable lithium-ion battery has average driver voltage as high as 3.6V, and is about 3 times the average driver voltage of the conventional nickel-cadmium battery or a nickel hydride battery. Since the mobility which participates in charge and discharge using a carbon material as negative electrode active material is lithium of a light metal, a weight saving can also expect this rechargeable lithium-ion battery.

[0003] In order unlike the nonaqueous secondary battery which uses conventional metal lithium as a negative electrode for this rechargeable lithium-ion battery to distribute the above-mentioned positive active material and negative electrode active material in a solvent with a binder etc., to consider it as a paste and to attain high capacity-ization, A band-like anode and negative electrode are produced by a positive pole collector and a negative pole collector applying the electrode compound content paste to the both sides, and drying and forming an electrode compound layer. And wind spirally the band-like anode and negative electrode which were obtained via a separator, and an electrode body is formed, After accommodating the electrode body in the sheathing material which consists of a laminate film which makes metallic foils, such as aluminium foil, a core material, and a battery can and pouring in an electrolysis solution, the cell is constituted by sealing.

[0004] By the way, high capacity-ization also with much more rechargeable lithium-ion battery used

as the power supply is desired with the increase in the power consumption by adding prolonged continuous use and functions, such as a cellular phone.

[0005]However, although theoretical service capacity is 274 mAh/g, typical  $\text{LiCoO}_2$  which is positive active material, If deep charge and discharge are performed, in order that  $\text{LiCoO}_2$  may cause a phase change and may reduce a cycle life, there is a problem that service capacity will become within the limits of 125 - 140 mAh/g in a actual rechargeable lithium-ion battery.

[0006]Although theoretical service capacity is 274 mAh/g like  $\text{LiCoO}_2$ , the above-mentioned  $\text{LiCoO}_2$  and  $\text{LiNiO}_2$  which is one sort of a lithium content multiple oxide similarly, Since the action potential on the basis of Li pole is low compared with  $\text{LiCoO}_2$  and it is not so rapid as the case where the voltage drop in the discharge last stage is  $\text{LiCoO}_2$ , The service capacity in 3.0 - 4.0V field is large compared with  $\text{LiCoO}_2$  to Li pole, and the service capacity in the potential range (it is a field of 3.0-4.3V to Li pole) in which the  $\text{LiNiO}_2$  is more practical than  $\text{LiCoO}_2$  is large. Although the service capacity in 3.0 to actual Li pole - 4.3V field changes also with synthetic conditions, generally in  $\text{LiNiO}_2$ , it is 160 - 200 mAh/g.

[0007]Therefore, the rather than direction which used  $\text{LiNiO}_2$  is expected that the cell of high capacity is more producible, using  $\text{LiCoO}_2$  as positive active material. Since the true density is 4.6 - 4.8 g/cm and restoration nature almost comparable as  $\text{LiCoO}_2$  is obtained, even if  $\text{LiNiO}_2$  replaces  $\text{LiCoO}_2$  by  $\text{LiNiO}_2$ , it does not almost have that restoration nature is inferior at the time of electrode production.

[0008]However, in order that the Ni ions which  $\text{LiNiO}_2$  tended to mix Ni ions (nickel<sup>+</sup>) between layers according to a synthetic condition etc., and were mixed between this layer may check movement of Li ion, the electrochemical capacity of  $\text{LiNiO}_2$  decreases. Since it was necessary to control composition of  $\text{LiNiO}_2$  by the bottom of oxygen environment carefully,  $\text{LiNiO}_2$  also had the problem that a manufacturing cost became high from  $\text{LiCoO}_2$ .

[0009]Although theoretical service capacity is 148 mAh/g,  $\text{LiMn}_2\text{O}_4$ , This  $\text{LiMn}_2\text{O}_4$  as well as  $\text{LiCoO}_2$  causes a phase change during charge and discharge, Since it is [ the true density of  $\text{LiMn}_2\text{O}_4$  ] small compared with 4.0 - 4.2 g/cm and  $\text{LiCoO}_2$ , when restoration nature is taken into consideration to the true density of  $\text{LiCoO}_2$  being 4.9-5.1g/cm, disadvantage will be produced also in respect of the capacity per volume.

[0010]As mentioned above, although  $\text{LiCoO}_2$ ,  $\text{LiNiO}_2$ , and  $\text{LiMn}_2\text{O}_4$  have the strong point and a fault, in order to attain high capacity-ization using them, it is thought, respectively that they need to raise restoration nature by diameter[ of a granule ]-izing or improvement in tap density in any case.

[0011]When producing an anode, to positive active material, such as  $\text{LiCoO}_2$ , by the way, an electronic conduction auxiliary agent, After applying the positive electrode mixture content paste which added and carried out mixture dispersion of a binder and the solvent, and prepared them on the positive pole collector which serves as the operation as a base, drying and forming a positive electrode mixture layer, in order to attain high capacity-ization, it presses and the thickness of a positive electrode mixture layer is adjusted. In order to raise the capacity per volume of an anode, it is necessary to make density of a positive electrode mixture layer high. However, since osmosis of an electrolysis solution will be controlled if press pressure is made high and improvement in density is aimed at, there is a problem that the fall of capacity arises at the time of charge and discharge, or a cycle characteristic worsens.

[0012]On the other hand, improving a battery characteristic is proposed also from the former by adding a surface-active agent in an anode, a negative electrode, or an electrolysis solution (JP,H05-335018,A, JP,H07-263027,A).

[0013]However, in the method proposed in the above-mentioned gazette, since mixture dispersion of the surface-active agent is carried out with negative electrode active material and a binder or the surface-active agent is added before [ after forming a positive electrode mixture layer ] a press, it has not contributed to high restoration-ization of positive active material at all. In order to prepare positive electrode mixture in solution, when it is necessary to dry at the elevated temperature which exceeds 200 \*\* to make removal of moisture perfect, therefore polyvinylidene fluoride is used, for example as a binder, there is a possibility of promoting the defluoric acid reaction of polyvinylidene fluoride at the time of desiccation.

[0014]

[Problem(s) to be Solved by the Invention]This invention solves the problem in the above conventional technologies, attains high restoration-ization of positive active material, and an object of this invention is to provide the nonaqueous secondary battery which is high capacity and in which the charge-discharge cycle characteristic was excellent.

[0015]

[Means for Solving the Problem]In a nonaqueous secondary battery which has at least one anode, negative electrode, and \*\*\*\*\* of a positive pole collector which form a positive electrode mixture layer in a field as a result of repeating research wholeheartedly, in order that this invention persons may solve an aforementioned problem, By making a fluorine system Nonion type surface-active agent contain in the above-mentioned positive electrode mixture, it finds out that an aforementioned problem is solvable and came to complete this invention.

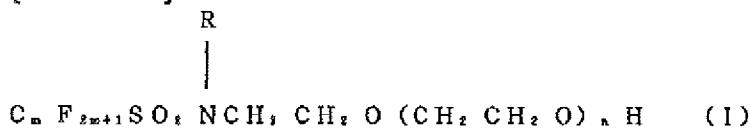
[0016]Especially the positive electrode mixture content paste that added and carried out mixture dispersion of the fluorine system Nonion type surface-active agent to a system containing positive active material, a binder, and an organic solvent, and prepared it in it can attain much more high restoration-ization of positive active material. Since a fluorine system Nonion type surface-active agent sticks to the surface of positive active material, such as cobalt acid lithium, and positive active material distributes this with a binder, high distribution of positive active material is attained

compared with a case where a fluorine system Nonion type surface-active agent is not added. Therefore, if it has added a fluorine system Nonion type surface-active agent in applying, drying and pressing under the same conditions and forming a positive electrode mixture layer, compared with a case where a fluorine system Nonion type surface-active agent is not added, high restoration-ization of an active material in a positive electrode mixture layer can be attained. Since positive active material is distributing to homogeneity more in a positive electrode mixture layer, stability to a repetition of charge and discharge also becomes high.

[0017]

[Embodiment of the Invention] Various kinds of things can be used for a fluorine system Nonion type surface-active agent in this invention, without being limited especially if it is the Nonion type surface-active agent which has a fluoro group. For example, as a hydrophobic group of the fluorine system Nonion type surface-active agent, a perfluoroalkyl group, a perfluoro alkylphenyl group, a perfluoro phenyl group, etc. are mentioned, and a polyethylene oxide chain, a poly oxazoline chain, etc. are mentioned as a hydrophilic portion. Especially a desirable thing is following formula (I).

[Formula 2]



It is a compound by which expresses (m with the integer of 4-12, n is expressed with the integer of 5-30, and R is expressed with low-grade alkyl group).

[0018] In the above-mentioned formula (I), although m is an integer of 4-12, it is for this attaining high restoration-ization of positive active material, controlling the rise of the viscosity of a positive electrode mixture content paste by making m or less into 12, and raising the dispersibility of positive active material by making m or more into four. It is for maintaining this at the viscosity which raised the dispersibility of positive active material, controlled the rise of the viscosity of a positive electrode mixture content paste by making n or less into 30, and was suitable for spreading by making n or more into five into the above-mentioned formula (I), although n is an integer of 5-30.

[0019] And in the above-mentioned formula (I), R is a low-grade alkyl group, generally this low-grade alkyl group is an alkyl group of the carbon numbers 1-5, and there is F142 by Dainippon Ink & Chemicals, Inc. (trade name), etc., for example as a commercial item of the fluorine system Nonion type surface-active agent belonging to this range. And the fluorine system Nonion type surface-active agent expressed with the above-mentioned formula (I) can make the effect of this invention reveal notably especially by adding in the system containing positive active material, a binder, and an organic solvent.

[0020] As for a fluorine system Nonion type surface-active agent, it is preferred to make it contain 0.01 to 1% of the weight in positive electrode mixture, By carrying out the content to 0.01% of the weight or more, an effect of addition of a fluorine system Nonion type surface-active agent is made

to fully reveal, by carrying out to 1 or less % of the weight, a rise of viscosity of a positive electrode mixture content paste can be controlled, and the dispersibility of positive active material can be raised.

[0021]In this invention, although not limited especially as positive active material, For example, lithium manganic acid ghosts, such as lithium cobalt oxides, such as  $\text{LiCoO}_2$ , and  $\text{LiMn}_2\text{O}_4$ , Lithium nickel oxides, such as  $\text{LiNiO}_2$ , manganese dioxide, A multiple oxide which makes basic structure metallic oxides, such as vanadium pentoxide and a chromium oxidation thing, or them. It is independent or metallic sulfide, such as (for example, a dissimilar metal addition article) or titanium disulfide, and molybdenum disulfide, etc. can be used as two or more sorts of mixtures, or those solid solutions.

[0022]When open circuit voltage at the time of charge of  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ ,  $\text{LiMn}_2\text{O}_4$ , etc. uses especially a lithium containing compound metal oxide in which more than 4V is shown on Li standard as positive active material, since high energy density is obtained, it is desirable. In using  $\text{LiMn}_2\text{O}_4$  with the lowest true density also in it, a high restoration-ized effect by addition of a

fluorine system Nonion type surface-active agent of this invention is notably revealed especially.

[0023]An anode to the above-mentioned positive active material if needed, for example And scaly graphite, In a system which adds electronic conduction auxiliary agents and binders, such as carbon black, and in which an organic solvent exists. Mixture dispersion of said fluorine system Nonion type surface-active agent is added and carried out, and a positive electrode mixture content paste is prepared (in preparation of a positive electrode mixture content paste). . Since it is made to dissolve in a solvent beforehand, a binder may be mixed with positive active material etc. An obtained positive electrode mixture content paste is applied to a positive pole collector which serves as an operation as a base, it dries, a positive electrode mixture layer is formed in at least one field of a positive pole collector, and it is produced through a process of pressurizing and compressing the positive electrode mixture layer. However, a manufacturing method of an anode is good by other methods, without being restricted to a method of the above-mentioned illustration.

[0024]As a binder used in production of the above-mentioned anode, kinds of polymer and polysaccharide which have thermoplastics and rubber-like elasticity, or those mixtures can be used, for example. Polyvinylidene fluoride system resin, such as a copolymer which uses polyvinylidene fluoride and vinylidene fluoride as a principal member as the example, for example, Polytetrafluoroethylene, polyethylene, polypropylene, ethylene-propylene-diene copolymerization resin, Cellulose type resin, such as styrene butadiene rubber, polybutadiene, fluorocarbon rubber, polyethylene oxide, a polyvinyl pyrrolidone, polyester resin, an acrylic resin, phenol resin, an epoxy resin, polyvinyl alcohol, and hydroxypropylcellulose, etc. are mentioned. When using also in them polyvinylidene fluoride system resin, such as a copolymer which uses polyvinylidene fluoride and vinylidene fluoride as a principal member, as a binder of an anode, an effect of this invention can be made to reveal notably especially.

[0025]In this invention, although foil of metal, such as aluminum, nickel, copper, and stainless

steel, a net, a punching metal, an expanded metal, etc. can use as a charge collector used in production of the above-mentioned anode, especially as a positive pole collector, aluminium foil is used suitably. Especially as thickness of the above-mentioned positive pole collector, 5-60 micrometers, 8-40 micrometers is preferred, and thickness of a positive electrode mixture layer formed in at least one field of the positive pole collector is the stage pressurized and compressed, and 50-150 micrometers is especially preferred [ thickness ] 30-300 micrometers per one side.

[0026]As a material used for a negative electrode, a dope and a substance which can be dedoped are called [ be / what is necessary / it can dedope and / just a dope and in this invention for a lithium ion ] negative electrode active material for such a lithium ion. And especially as this negative electrode active material, although not limited. For example, black lead, pyrolytic carbon, corks, glassy carbon, a baking body of an organic polymer compound, Oxides etc. which can carry out charge and discharge by a low voltage near an alloy or Li(s), such as carbon materials, such as meso carbon micro beads, carbon fiber, and activated carbon, Si, Sn, and In, such as Si, Sn, and In, can be used.

[0027]When using a carbon material as negative electrode active material, what has the following characteristic as this carbon material is preferred. That is, about a spacing ( $d_{002}$ ) of the (002) field, 0.35 nm or less is preferred, and 0.345 nm or less is 0.34 nm or less still more preferably more preferably. About a size ( $L_c$ ) of microcrystal of c shaft orientations, not less than 3.0 nm is preferred, and not less than 8.0 nm is not less than 25.0 nm still more preferably more preferably. And as for especially mean particle diameter of the above-mentioned carbon material, 10-15 micrometers is preferred 8-20 micrometers, and 99.9 % of the weight or more of purity is preferred.

[0028]If a negative electrode adds the same binder as a case of said anode to the above-mentioned negative electrode active material and it takes it further to it if needed, for example, an electronic conduction auxiliary agent will be added, Paste state is used with a solvent (since it is made to dissolve in a solvent beforehand, a binder may be mixed with negative electrode active material etc.), An obtained negative-electrode-active-material content paste is applied to a negative pole collector which has the operation as a base, it dries, a negative electrode mixture layer is formed, and it is produced by passing through a process of pressurizing and compressing the negative electrode mixture layer. However, a manufacturing method of a negative electrode is good by other methods, without being restricted to a method of the above-mentioned illustration.

[0029]It is requested that what is suitable for high capacity-ization also about negative electrode active material is especially used with a future nonaqueous secondary battery, Concern about a nonaqueous secondary battery using a graphite material (henceforth "natural graphite material") in which crystallinity is high and service capacity has natural graphite and a natural graphite gestalt of high capacity of 350 or more mAh/g also in a carbon material as negative electrode active material is increasing. However, in the case of natural graphite material of those high capacity, compared with the usual artificial-graphite material, an interaction between adhesive strength to a negative pole collector or those black lead is weak, and, as for a nonaqueous secondary battery produced

using it as negative electrode active material, it has left SUBJECT to a cycle characteristic. In order to solve such SUBJECT, in a negative pole material which used natural graphite material, Carboxyl group containing polymer and bridge construction material which contains two or more epoxy groups in intramolecular are made to contain, By applying a negative electrode mixture content paste containing them to a negative pole collector, carrying out stoving, making a carboxyl group and an epoxy group in carboxyl group containing polymer react, and carrying out three-dimensional bridge construction, A nonaqueous secondary battery which has a binding property between negative electrode active material, high adhesive strength of a negative pole collector and a negative electrode mixture layer, and few falls of cell capacity accompanying a repetition of charge and discharge and which was excellent in a cycle characteristic comes to be obtained.

[0030]As the above-mentioned carboxyl group containing polymer, For example, fluororesin, an epoxy resin, phenol resin, polyester resin, Thermoplastics, such as silicone resin, an acrylic resin, allylic resin, and butadiene resins, What what contains a carboxyl group by polymer etc. which have rubber elasticity is independent respectively, or can use as two or more sorts of mixtures, and contains a carboxyl group with fluororesin also in them is preferred.

[0031]As content of a carboxyl group in the above-mentioned carboxyl group containing polymer, more than 0.1mol% is preferred among [ from a point of crosslinking density ] polymer, and more than 0.5mol% is more preferred, and less than 80mol% is preferred, and less than 30mol% is more preferred.

[0032]And although it changes also with kinds of polymer as a number average molecular weight of the above-mentioned carboxyl group containing polymer, 10,000 or more are preferred, and 100,000 or more are more preferred, and 1 million or less are preferred, and 500,000 especially or less are more preferred.

[0033]Bridge construction material which contains the two or more above-mentioned epoxy groups in intramolecular, Are for making the above-mentioned carboxyl group containing polymer construct a bridge, and as an example of such bridge construction material, For example, glycidyl amine, glycidyl ether, glycidyl ester, glycidyl amine and a cyclic aliphatic compound (a cyclohexene oxide group.) Only when a compound etc. which have a tricyclo decene oxide group, a cyclopentene oxide group, etc. are mentioned, it exists stably at a room temperature also in them and a negative electrode is heat-treated, glycidyl amine is the most preferred at a point that it can react to a carboxyl group. As a commercial item of a thing belonging to such glycidyl amine, it is N,N,N' and N'-tetraglycidyl ether m-xylenediamine, for example. [Mitsubishi Gas Chemical [ Co., Inc. ] make: TETRAD-X(trade name)] 1,3-bis(N,N-diglycidyl aminomethyl)cyclohexane [Mitsubishi Gas Chemical [ Co., Inc. ] make: TETRAD-C(trade name)] \*\*\*\* is mentioned.

[0034]Also in order to increase a reactive site which can react to a carboxyl group as content of an epoxy group of bridge construction material which contains the two or more above-mentioned epoxy groups in intramolecular, it is required for intramolecular to be two or more pieces, and it is preferred that they are four or more pieces.

[0035]As the mixing ratio of bridge construction material contained two or more pieces in intramolecular, the above-mentioned carboxyl group containing polymer and an epoxy group, 0.2

or more equivalent ratio is preferred at equivalent ratio (equivalent of the equivalent/carboxyl group of an epoxy group) of an epoxy group to a carboxyl group, and 1 or more equivalent ratio is more preferred, and 20 or less equivalent ratio is preferred, and 10 or less equivalent ratio is more preferred. By making a ratio of an epoxy group into 0.2 or more equivalent ratio, when a reaction of a carboxyl group and an epoxy group is advanced properly and used as a bridging body, an electrical junction state between a negative electrode mixture layer and a negative pole collector at the time of charge and discharge can be raised, and a fall of cell capacity can be controlled. On the other hand, by making a ratio of an epoxy group into 20 or less equivalent ratio, elution to an electrolysis solution can be controlled, a fall of cell capacity can be controlled, and proper cell capacity can be secured. When using such a binder, a binder by which normal use is carried out to a nonaqueous secondary battery can be used together.

[0036]Although the same thing as a case of said positive pole collector can be used about that construction material and shape as a negative pole collector used in production of the above-mentioned negative electrode, especially as this negative pole collector, copper foil is suitable. And especially as thickness of the above-mentioned negative pole collector, as negative electrode mixture layer thickness formed in at least one field of the negative pole collector, it is the stage pressurized and compressed and 50-150 micrometers is especially preferred [ 8-40 micrometers is preferred, and ] 5-60 micrometers 30-300 micrometers per one side.

[0037]As a coating method at the time of applying the above-mentioned positive-active-material content paste and a negative-electrode-active-material content paste to a charge collector, various kinds of coating methods including an extrusion coating machine, a reverse roller, a doctor blade, etc. can be adopted in production of the above-mentioned anode or a negative electrode, for example.

[0038]Although both a liquid electrolyte a gel polymer electrolyte and a solid electrolyte can be used as nonaqueous electrolyte in this invention, since a liquid electrolyte is used, in the following, this liquid electrolyte is usually explained in detail focusing on it using the expression an "electrolysis solution."

[0039]In this invention, an electrolysis solution is prepared by dissolving electrolyte salt, such as lithium salt, in nonaqueous solvents, such as an organic solvent, for example. And as the solvent, ester is used suitably. Especially chain ester lowers viscosity of an electrolysis solution, and is suitably used from raising ionic conductivity. As such chain ester, dimethyl carbonate, diethyl carbonate, Chain trialkyl phosphate, such as chain alkyl ester, such as chain carbonate, such as methylethyl carbonate, and methyl propionate, and trimethyl phosphate, etc. are mentioned, and chain carbonate is especially preferred also in them.

[0040]Since a load characteristic etc. will improve if ester (with a dielectric constant [ of 30 or more ] ester) with the following high dielectric constant is mixed and used for the above-mentioned chain ester etc., it is desirable. As ester with such a high dielectric constant, ethylene carbonate, propylene carbonate, butylene carbonate, gamma-butyrolactone, etc. are mentioned, for example. Especially a thing of cyclic structure is preferred, annular carbonate is especially preferred, and ethylene carbonate is the most preferred.

[0041]As a solvent which can be used together in addition to the above-mentioned ester, 1,2-dimethoxyethane, 1,3-dioxolane, a tetrahydrofuran, 2-methyl-tetrahydrofuran, diethylether, etc. are mentioned, for example. In addition, an amine system or an imide series organic solvent, a \*\* sulfur system or a fluorine-containing organic solvent, etc. can be used. And those solvents are independent respectively, or two or more sorts can be mixed and they can be used.

[0042]As electrolyte salt, such as lithium salt used in preparation of an electrolysis solution, For example,  $\text{LiClO}_4$ ,  $\text{LiPF}_6$ ,  $\text{LiBF}_4$ ,  $\text{LiAsF}_6$ ,  $\text{LiCF}_3\text{SO}_3$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$ ,  $\text{LiCF}_3\text{CO}_2$ ,  $\text{Li}_2\text{C}_2\text{F}_4(\text{SO}_3)_2$ ,  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ ,  $\text{LiC}(\text{CF}_3\text{SO}_2)_3$ ,  $\text{LiC}_n\text{F}_{2n+1}\text{SO}_3$  ( $n \geq 2$ ),  $\text{LiN}(\text{RfOSO}_2)_2$  [ -- here -- Rf -- fluoro alkyl group] Although it is independent, or two or more sorts of \*\*\*\* are mixed and are used,  $\text{LiPF}_6$ ,  $\text{LiC}_4\text{F}_9\text{SO}_3$ , etc. are especially preferred. Although concentration in particular of electrolyte salt, such as lithium salt in an electrolysis solution, is not limited, its 0.3 or more mol/l is preferred, and it is more preferred in 0.4 mol/l. or more, and itsl. is preferred in 1.7 mol /or less, and its 1.5 or less mol/l is more preferred.

[0043]Although a gel polymer electrolyte is equivalent to what gelled an electrolysis solution by a gelling agent, In the gelling, for example Polyvinylidene fluoride, polyethylene oxide, Straight-chain-shape polymer or those copolymers, such as polyacrylonitrile, Polyfunctional monomer polymer-ized by the exposure of active light, such as ultraviolet rays and an electron beam. for example, pentaerythritol tetraacrylate and ditrimethylolpropanetetraacrylate. Ethoxylation pentaerythritol tetraacrylate, dipentaerythritol hydroxy pentaacrylate, acrylate of four or more organic functions, such as dipentaerythritol hexaacrylate, and the above-mentioned acrylate, same methacrylate of four or more organic functions, etc. -- etc. -- it is used. However, in the case of a monomer, the monomer itself does not make an electrolysis solution gel, but polymer which polymer-ized the above-mentioned monomer acts as a gelling agent.

[0044]If required when making an electrolysis solution gel using polyfunctional monomer as mentioned above, As a polymerization initiator, for example Benzoyls and benzoin alkyl ether. Benzophenones, benzoylphenyl phosphine oxide, acetophenones, thioxan tons, and anthraquinone can be used, and alkylamine and aminoester can also be further used as a sensitizer of a polymerization initiator.

[0045]In this invention, a solid electrolysis solution can also be used as nonaqueous electrolyte in addition to the above-mentioned electrolysis solution (liquid electrolyte) or a gel polymer electrolysis solution. As the solid electrolyte, both an inorganic system solid electrolyte and an organic system solid electrolyte can be used.

[0046]In this invention, although a separator is made to intervene between the above-mentioned anode and a negative electrode, as the separator, a microporous resin film, a nonwoven fabric, etc. are usually used suitably, for example. As the above-mentioned microporous resin film material, polyethylene, polypropylene, a polyethylene propylene copolymer, etc. are mentioned and polypropylene, polyethylene, polyethylene terephthalate, polybutylene terephthalate, etc. are mentioned as the above-mentioned nonwoven fabric material, for example.

[0047]A nonaqueous secondary battery of this invention a spiral electrode body which made a separator intervene between an anode and a negative electrode which are produced as mentioned above, for example, and carried out winding production spirally, or a laminated laminated electrode body, After accommodating in a battery can made from iron and stainless steel which performed the inside of a sheathing material which comprises a laminate film which makes metallic foils, such as aluminium foil, a core material, and a nickel plate and pouring in an electrolysis solution, it is produced through a process to seal.

[0048]

[Example]Working example of this invention is described below. However, this invention is not limited only to those working example.

[0049]Production of working example 1 anode:  $2O_4LiMn_{180}$  weight section which is positive active material, acetylene black 10 weight section which is electronic conduction auxiliary agents, polyvinylidene fluoride 6 weight section which is binders, a fluorine system Nonion type surface-active agent [Dainippon Ink industrial company make, F142 (trade name)] 0.5 weight sections were mixed so that it might become uniform, and N-methyl-2-pyrrolidone 70 weight section was added further, it mixed, and the positive electrode mixture content paste was prepared. After passing the net of 70 meshes for the obtained positive electrode mixture content paste and removing a big thing, After having applied uniformly except for the portion used as a joined part with a lead body, drying to both sides of the positive pole collector which consists of 15-micrometer-thick aluminium foil and forming a positive electrode mixture layer in them, it pressurized with the linear pressure 198N, and overall thickness was compressed into 169 micrometers. Then, it cut to prescribed size, the lead body made from aluminum was welded to the exposed portion of the positive pole collector, and the sheet shaped anode was obtained. The density of the positive electrode mixture layer in this anode was  $2.8g/cm^3$ .

[0050]Production of a negative electrode: The black lead system carbon material as negative electrode active material [However, spacing ( $d_{002}$ ) =0.337nm of the 002nd page, size (Lc) =95.0nm of the microcrystal of c shaft orientations,

Black lead system carbon material 180 weight section with the characteristic of the mean particle diameter of 10 micrometers and not less than 99.9% of purity was mixed with the solution in which N-methyl-2-pyrrolidone 190 weight section was beforehand dissolved for polyvinylidene fluoride 14 weight section, and the negative electrode mixture content paste was prepared. After having applied uniformly the obtained negative-electrode-active-material content paste to both sides of the negative pole collector which consists of 10-micrometer-thick copper foil except for the portion used as a joined part with a lead body, drying and forming negative electrode mixture, with the above, it was at the same pressure, it pressurized, and overall thickness was compressed into 167 micrometers. Then, it cut to prescribed size, the end of the lead body made from nickel welded to the exposed portion of the negative pole

collector, and the sheet shaped negative electrode was obtained.

[0051]Preparation of an electrolysis solution: 1.2 mol LiPF<sub>6</sub> was dissolved in the mixed solvent which mixed ethylene carbonate and methylethyl carbonate by the volume ratio 1:2, and the electrolysis solution in which a presentation is shown by 1.2 mol/lLiPF<sub>6</sub>/EC:MEC (1:2 volume ratios) was prepared.

[0052]EC in the above-mentioned electrolysis solution is the abbreviation for ethylene carbonate, and MEC is the abbreviation for methylethyl carbonate. Therefore, 1.2-mol / lLiPF<sub>6</sub>/EC:MEC (1:2 volume ratios) which shows the above-mentioned electrolysis solution shows carrying out the 1.2 mol/l dissolution of the LiPF<sub>6</sub> to the mixed solvent of the volume ratio 1:2 of methylethyl carbonate and ethylene carbonate.

[0053]Production of a nonaqueous secondary battery: The above-mentioned anode was put on the above-mentioned negative electrode after the drying process via the separator which consists of a 25-micrometer-thick microporous polyethylene film, the above-mentioned anode and the negative electrode were wound spirally, and it was made the electrode body of spiral winding structure. After accommodating the electrode body of this spiral winding structure in metal battery cans and pouring in the above-mentioned electrolysis solution, obturated the opening of the battery can using the battery lid and the annular gasket, neglected it in that state for 3 hours, the electrolysis solution was made to fully permeate an anode, a negative electrode, and a separator, and the nonaqueous secondary battery was produced.

[0054]Production of working example 2 anode: 2 O<sub>4</sub>LiMn<sub>180</sub> weight section which is positive active material, acetylene black 10 weight section which is electronic conduction auxiliary agents, polyvinylidene fluoride 6 weight section which is binders, a fluorine system Nonion type surface-active agent [The Dainippon Ink & Chemicals, Inc. make, F472 (trade name)] 0.5 weight sections were mixed so that it might become uniform, and N-methyl-2-pyrrolidone 70 weight section was added further, it mixed, and the positive electrode mixture content paste was prepared. After passing the net of 70 meshes for the obtained positive electrode mixture content paste and removing a big thing, After having applied uniformly except for the portion used as a joined part with a lead body, drying to both sides of the positive pole collector which consists of 15-micrometer-thick aluminium foil and forming a positive electrode mixture layer in them, with the case of working example 1, it was at the same pressure, it pressurized, and overall thickness was compressed into 171 micrometers. The lead body made from aluminum was welded to the exposed portion of the positive pole collector after cutting to prescribed size, and the sheet shaped anode was obtained. The density of the positive electrode mixture layer in this anode was 2.75g/cm<sup>3</sup>. And the nonaqueous secondary battery was produced like working example 1 except having used this anode.

[0055]2 O<sub>4</sub>LiMn<sub>180</sub> weight section which is comparative example 1 positive active material, acetylene black 10 weight

section which is electronic conduction auxiliary agents, Polyvinylidene fluoride 6 weight section which is a binder was mixed so that it might become uniform, and N-methyl-2-pyrrolidone 70 weight section was added further, it mixed, and the positive electrode mixture content paste was prepared. After passing the net of 70 meshes for the obtained positive electrode mixture content paste and removing a big thing, After having applied uniformly except for the portion used as a joined part with a lead body, drying to both sides of the positive pole collector which consists of 15-micrometer-thick aluminium foil and forming a positive electrode mixture layer in them, with the case of working example 1, it was at the same pressure, it pressurized, and overall thickness was compressed into 178 micrometers. The lead body made from aluminum was welded to the exposed portion of the positive pole collector after cutting to prescribed size, and the sheet shaped anode was obtained. The density of the positive electrode mixture layer in this anode was  $2.65\text{g}/\text{cm}^3$ . And the nonaqueous secondary battery was produced like working example 1 except having used the above-mentioned anode.

[0056]Change of cell capacity when charge and discharge are repeated about each nonaqueous secondary battery of above-mentioned working example 1-2 and the comparative example 1 was measured. The result is shown in Table 1.

[0057]The measuring method of cell capacity repeated charge and discharge up to 300 cycles under the conditions which provide the current limiting circuit of 1C, perform charge with the constant voltage of 4.2V, and perform discharge until the inter-electrode voltage of a cell falls to 2.75V, and measured each service capacity at that time. And in the display to Table 1 of the result. Service capacity of 1 cycle eye of the cell of working example 1 is made into 100%, the relative value of the service capacity of 1 cycle eye of the service capacity of the 300 cycle eye of the cell of working example 1 to it and the cell of working example 2 and the comparative example 1 and a 300 cycle eye is calculated, and it is displayed on Table 1 as service capacity (%).

[0058]

[Table 1]

	正極活物質	正極合剤層の密度 (g/cm <sup>3</sup> )	放電容量 (%)	
			1サイクル目	300 サイクル目
実施例1	L <sub>1</sub> Mn <sub>2</sub> O <sub>4</sub>	2. 8 0	1 0 0	9 2
実施例2	L <sub>1</sub> Mn <sub>2</sub> O <sub>4</sub>	2. 7 5	9 7	9 0
比較例1	L <sub>1</sub> Mn <sub>2</sub> O <sub>4</sub>	2. 6 5	9 2	7 9

[0059]So that clearly [ the cell of working example 1-2 may have the high service capacity of 1 cycle eye compared

with the cell of the comparative example 1 and ] from contrast with the service capacity of 1 cycle eye, and the service capacity of a 300 cycle eye, as shown in Table 1, There were few falls of the cell capacity accompanying a charging and discharging cycle, and the charge-discharge cycle characteristic was excellent. As shown in Table 1, the cell of working example 1-2 had the high density of the positive electrode mixture layer compared with the cell of the comparative example 1, but. In spite of the cell of working example 1-2 and the cell of the comparative example 1 being at the same pressure and pressurizing them in production of an anode, It is because high restoration-ization of positive active material was attained by the cell of working example 1-2 that the density of the positive electrode mixture layer of the cell of working example 1-2 became higher than the density of the positive electrode mixture layer of the cell of the comparative example 1 by having made the fluorine system Nonion type surface-active agent contain in positive electrode mixture. And it is thought that it is a factor whose charge-discharge cycle characteristic capacity is [ having attained high restoration-ization of positive active material, having made thickness of the positive electrode mixture layer thin, and having attained densification ] high as a battery characteristic, and came to be excellent in the cell of working example 1-2 as mentioned above.

[0060]  $\text{LiCoO}_2$  162 weight section which is working example 3 positive active material, acetylene black 10 weight section which is electronic conduction auxiliary agents, polyvinylidene fluoride 6 weight section which is binders, a fluorine system Nonion type surface-active agent [The Dainippon Ink & Chemicals, Inc. make, F142 (trade name)] 0.5 weight sections were mixed so that it might become uniform, and N-methyl-2-pyrrolidone 70 weight section was added further, it mixed, and the positive electrode mixture content paste was prepared. After passing the net of 70 meshes for the obtained positive electrode mixture content paste and removing a big thing, After having applied uniformly except for the portion used as a joined part with a lead body, drying to both sides of the positive pole collector which consists of 15-micrometer-thick aluminium foil and forming a positive electrode mixture layer in them, with the case of working example 1, it was at the same pressure, it pressurized, and overall thickness was compressed into 165 micrometers. The lead body made from aluminum was welded to the exposed portion of the positive pole collector after cutting to prescribed size, and the sheet shaped anode was obtained. The density of the positive electrode mixture layer in this anode was  $3.25\text{g/cm}^3$ . And the nonaqueous secondary battery was produced like working example 1 except having used the above-mentioned anode.

[0061]  $\text{LiCoO}_2$  162 weight section which is comparative example 2 positive active material, acetylene black 10 weight section which is electronic conduction auxiliary agents, Polyvinylidene fluoride 6 weight section which is a binder was mixed so that it might become uniform, and N-methyl-2-pyrrolidone 70 weight section was added further, it mixed, and the positive electrode mixture content paste was prepared. After passing the net of 70 meshes for the obtained positive

electrode mixture content paste and removing a big thing, After having applied uniformly except for the portion used as a joined part with a lead body, drying to both sides of the positive pole collector which consists of 15-micrometer-thick aluminium foil and forming a positive electrode mixture layer in them, with the case of working example 1, it was at the same pressure, it pressurized, and overall thickness was compressed into 175 micrometers. The lead body made from aluminum was welded to the exposed portion of the positive pole collector after cutting to prescribed size, and the sheet shaped anode was obtained. The density of the positive electrode mixture layer in this anode was  $3.15\text{g}/\text{cm}^3$ . And the nonaqueous secondary battery was produced like working example 1 except having used the above-mentioned anode.

[0062]Also about the cell of above-mentioned working example 3 and the comparative example 2, a 300 cycle repetition and service capacity were measured for charge and discharge under the same conditions as said working example 1. The result is shown in Table 2. However, in the display to Table 2 of the result. Service capacity of 1 cycle eye of the cell of working example 3 is made into 100%, the relative value of the service capacity of the 100 cycle eye of the cell of working example 3 and the service capacity of 1 cycle eye of the cell of the comparative example 2 and a 300 cycle eye over it is calculated, and it is displayed on Table 2 as service capacity %.

[0063]

[Table 2]

	正極活物質	正極合剤層の密度 ( $\text{g}/\text{cm}^3$ )	放電容量 (%)	
			1サイクル目	300サイクル目
実施例3	$\text{LiCoO}_2$	3.25	100	93
比較例2	$\text{LiCoO}_2$	3.15	96	76

[0064]As shown in Table 2, the cell of working example 3 had few falls of the cell capacity accompanying a charging and discharging cycle compared with the cell of the comparative example 2 so that clearly [ the service capacity of 1 cycle eye might be large and ] from contrast with the service capacity of 1 cycle eye, and the service capacity of a 300 cycle eye. That is, the cell of working example 3 which made the anode contain a fluoride Nonion type surface-active agent is high capacity compared with the cell of the comparative example 2 which is not making the fluoride Nonion type surface-active agent contain.

And the charge-discharge cycle characteristic was excellent.

As shown in Table 2, the density of the positive electrode mixture layer of the cell of working example 3 was higher

than the density of the positive electrode mixture layer of the cell of the comparative example 2, but. This as well as the case of the cell of working example 1-2 is depended on high restoration-ization of positive active material having been attained by the cell of working example 3 by having made the fluorine system Nonion type surface-active agent contain in the positive electrode mixture.

[0065]

[Effect of the Invention]it explained above -- as -- this invention -- high-capacity-izing -- and the nonaqueous secondary battery excellent in the charge-discharge cycle characteristic was able to be provided.

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[Translation done.]